# Blowdown of hydrocarbons pressure vessel with partial phase separation

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**Abstract**

We propose a model for the simulation of the blowdown of vessels containing two-phase (gas-liquid) hydrocarbon fluids, considering non equilibrium between phases. Two phases may be present either already at the beginning of the blowdown process (for instance in gas-liquid separators) or as the liquid is formed from flashing of the vapor due to the cooling induced by pressure decrease. There is experimental evidence that the assumption of thermodynamic equilibrium is not appropriate, since the two phases show an independent temperature evolution. Thus, due to the greater heat transfer between the liquid phase with the wall, the wall in contact with the liquid experiences a stronger cooling than the wall in contact with the gas, during the blowdown. As a consequence, the vessel should be designed for a lower temperature than if it was supposed to contain vapor only.

Our model is based on a compositional approach, and it takes into account internal heat and mass transfer processes, as well as heat transfer with the vessel wall and the external environment.

Numerical simulations show a generally good agreement with experimental measurements.

## 1 Introduction

The problems related to the blowdown of pressure vessels containing mixtures of hydrocarbons are well known amongst industries involved in plant designing and hydrocarbons extraction. In particular, the pressure and thermal stress to which the vessel

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is exposed during the blowdown can present a number of consequences such as cracks in the walls, that have to be predicted by an accurate simulation of the blowdown process. Problems are highly enhanced when some liquid is present in the vessel either already at the start of the depressurisation, or as a result of condensation of heavier hydrocarbons, induced by the cooling caused by the expansion. Clearly, being the depressurisation usually caused by security alerts, the blowdown process is often very rapid. Typically the pressure can fall by 100 bar in a few hundreds seconds. Depending on the concentration of the mixture of hydrocarbons, the fluid temperature can fall of as much as 100 K in the same time. In the case of presence of condensed liquid, the vessel wall in contact with it, as an effect of the higher thermal conductivity of the liquid, compared to the one of the gas, can be exposed to a temperature drop of almost as much as the liquid itself, *i.e.*, 50-100 K in a few minutes [7]. With these extreme working conditions, the modeling of the blowdown process have to be made by taking into account as many factors as possible. These include heat transfer with the external environment, the presence of many components in the vessel and the possibility of situations in which the assumption of phase equilibrium are not appropriate. In fact, in particular this aspect, which is comforted by experimental evidence [7], is usually not considered in thermodynamic commercial programs. Furthermore, the complexity of the thermodynamic behavior caused by the presence of many different hydrocarbons, rather than one pure fluid, often induce authors to neglect it in first approximation [11]. As far as we know, the only complete model analysed in the past is the one described by Haque *et al.* [8]. There, the authors claim their model to allow for a multicomponent system, non-equilibrium conditions between the gas and the liquid within the vessel, and possibility of having separate water as well as gas and liquid phase. Also all the heat transfers, except for the one between the two fluids, are taken into account of. However, despite the numerical results obtained by the authors show a good agreement with some experiments [7], the model is completely undocumented. A full understanding of the actual process and the mathematics involved is therefore, at present, beyond reach.

For these reasons, and with the financial and technical support of ENI S.p.A., a leading company involved in pipelines and fuels, we develop a complete model taking into account of all the factors above. Being interested in the evolution of the pressure within the vessel and the temperature of the fluids and the walls in contact with them, we neglect all the spatial variations of the thermodynamic quantities and concentrate on their evolution in time. The assumption of homogeneous fluid is consistent with what is actually measured experimentally during the blowdown, and therefore a priori justified by the necessity to focus on average quantities, rather than on their local variations. Furthermore, even a rapid blowdown process, occurs at a time-scale which is generally much longer than the time needed for the pressure within the vessel to rearrange. Therefore, local variations of the pressure should generally be neglected in a vessel. This is not as clear for the rearrangement of the temperature within the fluids. However, given the violence of the pressure drop, especially in the early stages of the depressurisation, the liquid, if present, will quickly start boiling strongly. This justifies, through a strong convection, the homogeneity of its temperature. For the gas, on the other hand, assuming a rapid motion induced by the acceleration of the gas far upstream the orifice towards the exit, we can imagine it to get mixed and homogenized at all the time, especially in the early stages of the blowdown, while the pressure is dropping steeply.

Our model is only partially based on the description of the model by Haque et al. in [8]. In fact, it differs from it rather deeply in the treatment reserved to the

energy balance. Furthermore, we neglect the presence of separate water and take into account the heat exchanged at the interface between the fluids. Here we underline the assumptions made, the basic equations, and the numerical scheme used to solve the model. In order to account for the mass exchanged between the gas and the liquid phase, in conditions away from the thermodynamic equilibrium, we introduce the "partial phase equilibrium assumption" that we describe in Sec. 2.

## 2   The model for mixtures of hydrocarbons

As we mentioned in the introduction, in spite of the observed the non-equilibrium conditions between the two phases (gas and liquid), possibly present in the vessels during the blowdown process, we have mass exchange between them. This means we have phase transition in one or both senses. In reality, being a globally non-equilibrium problem, it will be just the material at the interface between the two phases actually exhibiting the phase transition in either senses. However, since, as we mentioned, we neglect spatial variations of temperature and pressure, we will have to assume some kind of phase equilibrium between the two phases, in order to solve the problem of mass exchange. In order to do this, besides the two bulk phases gas "G" and liquid "L", we will introduce two intermediate phases, present instantly only in traces in the vessel, which are responsible for the phase transition between the two bulk phases. We will call these two phases, drops "l", *i.e.*, the liquid that condenses from the gas and that, immediately after condensation falls into the bulk liquid, and vapor "g", which is the gas that vaporizes from the bulk liquid phase, and that migrates into the bulk gas region, immediately after forming.

Since the two bulk phases are in non-equilibrium conditions, *i.e.*, at different temperatures $T^{\mathrm{G}}$ and $T^{\mathrm{L}}$, while the two incipient phases "l" and "g" has to be in equilibrium with their respective parent phases "G" and "L", we will assume $T^{\mathrm{l}} = T^{\mathrm{G}}$ and $T^{\mathrm{g}} = T^{\mathrm{L}}$. Thus, as the incipient phases move into their respective bulk phases (g moves into L and l moves into G) they slightly influence their temperatures, as they mix with them. On the other hand, the two incipient phases mix with the two bulk phases, and thus, they homogenize with them.

We will call the assumption above, "partial phase equilibrium", since we assume that the two incipient (daughter) phases are instantly in equilibrium with their respective parents. However, as soon as they move into their bulk phases, they mix with them and disappear. This process is repeated all the time, as long as phase transition occurs, in either sense. Clearly, not necessarily the transition will be present in both senses. In fact, likely only vaporization will occur in most of the cases. Then, only "g" will be present in the vessel. However, as temperature drops due to expansion, the heavier components of the gas might condense, making the phase transition run in both directions.

Let us then proceed to the underline of the full model for a multicomponent system. Since it would lead us beyond the scope of the present work, here we will not derive the form of basic equations of the model. However, for a clear derivation and general considerations on the basic assumptions made, we will refer the reader to good descriptions of the experimental setting and the basic model, by Dutton and co-workers [3, 2].

## 2.1 Polydisperse mass and energy balance

Our model, is based on the mass and energy balance equations, between the two bulk phases G and L. Since the two daughter phases appear and disappear all the time, and are instantly present just in traces in the vessel, we will not consider them in the global balance, but they will appear as source terms for the balance equations.

Let us introduce $n_i^a$, the number of moles of component $i$ in each phase (G and L) and $\psi_i^{\mathrm{out}}$, the function describing the discharge [1] of component $i$. Let us also introduce $\psi_i^{\mathrm{vap}}$ and $\psi_i^{\mathrm{cond}}$, as the functions describing the rate of vaporization (*i.e.* the number of moles of component $i$ moving from L to g per unit time) and condensation (*i.e.* the number of moles of component $i$ passing from G to l per unit time) of component $i$, respectively.

Since the internal energy and enthalpy are written for the phase, and not for the single species, we will write just two energy balance equations, while we will write one equation for each species and each phase (G and L) for the number of moles (mass balance). Assuming we have M components, we will therefore have

$$\frac{dn_i^{\mathrm{G}}}{dt} = -\psi_i^{\mathrm{out}} + \psi_i^{\mathrm{vap}} - \psi_i^{\mathrm{cond}} \tag{1}$$

$$\frac{dn_i^{\mathrm{L}}}{dt} = -\psi_i^{\mathrm{vap}} + \psi_i^{\mathrm{cond}} \tag{2}$$

$$\text{for} \quad i = 1 \ldots \mathrm{M}$$

From the 2M equations above we will get the evolution of $n_i^{\mathrm{G}}$ and $n_i^{\mathrm{L}}$ due to the discharge and the net balance between condensation and vaporization.

The energy balance is, on the other hand, simply

$$\frac{d}{dt}\left(n^{\mathrm{G}} u^{\mathrm{G}}\right) = -h^{\mathrm{G}}\psi^{\mathrm{out}} - h^{\mathrm{G}}\psi^{\mathrm{cond}} - \left(h^{\mathrm{l}} - h^{\mathrm{G}}\right)\psi^{\mathrm{cond}} + h^{\mathrm{g}}\psi^{\mathrm{vap}}$$
$$+ \lambda_{\mathrm{LG}} S_{\mathrm{LG}}(T^{\mathrm{L}} - T^{\mathrm{G}}) + \lambda_{\mathrm{WG}} S_{\mathrm{WG}}(T^{\mathrm{WG}} - T^{\mathrm{G}}) \tag{3}$$

$$\frac{d}{dt}\left(n^{\mathrm{L}} u^{\mathrm{L}}\right) = h^{\mathrm{l}}\psi^{\mathrm{cond}} - h^{\mathrm{L}}\psi^{\mathrm{vap}} - \left(h^{\mathrm{g}} - h^{\mathrm{L}}\right)\psi^{\mathrm{vap}}$$
$$- \lambda_{\mathrm{LG}} S_{\mathrm{LG}}(T^{\mathrm{L}} - T^{\mathrm{G}}) + \lambda_{\mathrm{WL}} S_{\mathrm{WL}}(T^{\mathrm{WL}} - T^{\mathrm{L}}) \tag{4}$$

where the global quantities are simply obtained by summing the single species quantities; for instance, $\psi^{\mathrm{vap}} = \sum_i \psi_i^{\mathrm{vap}}$. Here $S_{\mathrm{LG}}$ is just the area of the interface between the two phases and $S_{\mathrm{WL}}$ and $S_{\mathrm{WG}}$ is the area of interface between the phases and the wall in contact with them, while the $\lambda$ coefficients are just the thermal exchange coefficients between the two phases and the phases and the walls in contact with them [9, 6, 4, 5].

To the 2M+2 above equations, we will add the obvious total volume conservation

$$V_0 = n^{\mathrm{G}} v^{\mathrm{G}} + n^{\mathrm{L}} v^{\mathrm{L}} \tag{5}$$

and the four equations of state, one for each phase (see below), for a total of 2M+7 equations in the 2M+7 unknowns $n_1^{\mathrm{G}} \ldots n_{\mathrm{M}}^{\mathrm{G}}$, $n_1^{\mathrm{L}} \ldots n_{\mathrm{M}}^{\mathrm{L}}$, $v^{\mathrm{G}}$, $v^{\mathrm{L}}$, $v^{\mathrm{l}}$, $v^{\mathrm{g}}$, $P$, $T^{\mathrm{G}}$, $T^{\mathrm{L}}$. The two quantities $T^{\mathrm{WL}}$ and $T^{\mathrm{WG}}$ are obtained by solving the two Fourier equations across the wall, coupled with the system above.

## 2.2 Polydisperse phase equilibrium

Since the hydrocarbons have different molecular weight, the rate of condensation and vaporization will be different from species to species, as different different is their tendency to be in the gas or liquid phase (expressed in formal terms by their chemical potentials). Different will also be the discharge rate, $\psi_i^{\text{out}}$, since as we can imagine, generally the lighter components will tend to stay in the top part of the vessel and thus closer to the orifice. Especially in the early stages of the blowdown, we can therefore imagine the gas phase to lose part of its lighter components. However, we will neglect this aspect and we will assume simply that $\psi_i^{\text{out}} = x_i^{\text{G}} \psi^{\text{out}}$, where $x_i^a = n_i^a / \sum_j n_j^a$ is the mole fraction of species $i$ in the phase $a$ (the sum is extended to M) and $\psi^{\text{out}}$ is the total discharge rate. In other words, we will assume the gas to be perfectly mixed, assumption which is actually consistent with the neglect of spatial variation of $P$ and $T$.

The values of $\psi_i^{\text{cond}}$ and $\psi_i^{\text{vap}}$ will be then obtained by solving the phase equilibrium conditions for the two sub-systems G↔l and L↔g, in which, in fact, we have split our system. Since we now have a multicomponent system, we will need to solve

$$\mu_i^{\text{G}} = \mu_i^{\text{l}} \ \Big| \ \mu_i^{\text{L}} = \mu_i^{\text{g}}$$

$$\text{for} \quad i = 1 \dots \text{M}$$

From the solution of the phase equilibrium conditions above, we will get $n_i^{\text{l}}$ and $n_i^{\text{g}}$ as functions of $P$, $T^{\text{G}}$, $T^{\text{L}}$ and the composition of the two parent phases[1] ($n_i^{\text{L}}$ and $n_i^{\text{G}}$). At fixed $t$ and thus at fixed $P(t)$ and $T^{\text{G}}(t)$ and $T^{\text{L}}(t)$, we will therefore need to solve the above phase equilibria to get $n_i^{\text{g}}$, $n_i^{\text{l}}$. The rate of condensation and vaporization are thus:

$$\psi_i^{\text{cond}} \quad = \quad \frac{dn_i^{\text{l}}}{dt} \tag{6}$$

$$\psi_i^{\text{vap}} \quad = \quad \frac{dn_i^{\text{g}}}{dt} \tag{7}$$

## 3  Numerical results

Here we will present just the results obtained with our model, relatively to two experiments (I1 and S9) reported in [7]. However, these are just two preliminary results, while we will apply our model to far more complex environments. In any case, it is useful to use our model in these two particular situations, since there Haque and co-workers describe the experimental apparatus and give some experimental results that can be directly compared with what we obtain from our model.

## 3.1  Experiment I1

The experiment consists on the blowdown of a cylindrical steel vessel, with base diameter 0.273 m, length 1.524 m, wall thickness 2.5 cm and top choke of diameter 0.635 cm. The vessel contains only $N_2$ at 150 bar and 290.15 K. The vessel is immersed in stagnant air at 290.15 K, thus everything is in equilibrium before opening the valve.

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[1] Note here that the parent depends on time, since there is some fractionation which is induced by the discharge of gas only. Since presumably the most volatile hydrocarbons will mainly be in gas phase, the discharge of gas only will leave only the heavier hydrocarbons in the vessel.

In Fig. 1(a) we report the value of the pressure inside the vessel during the blow-down, predicted and experimental. The agreement is rather good, besides a small deviation from the experimental data, roughly at half process. As can easily be seen on a logarithmic scale, the blowdown is almost exactly exponential. This is hardly surprising, being the conditions inside the vessel comparable to the ideal gas.
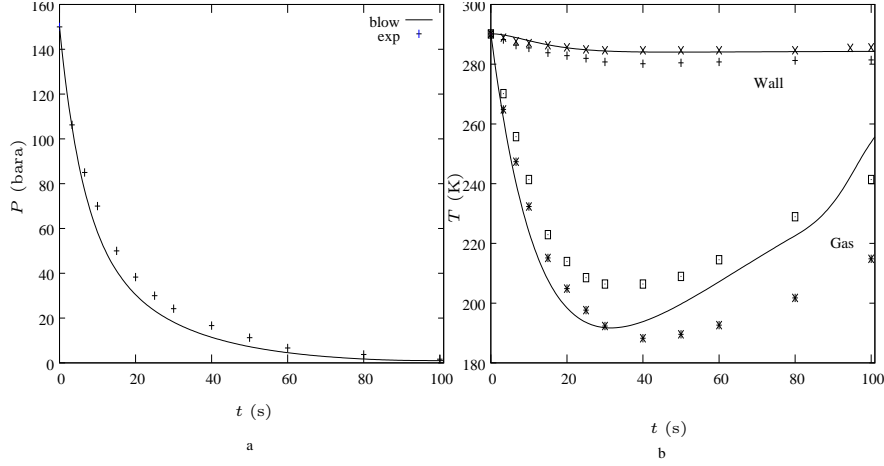


Fig. 1: a):Pressure behavior during experiment I1 obtained by our model *blow* and experimental results from Haque and co-workers. The agreement is rather good. b):Temperature of the gas and the wall in contact with it, obtained by our model, compared with the experimental results. Experimental results are contained between the two discontinuous curves. Again our numerical results lie between the two experimental curves.

In Fig. 1(b) we show the behavior of the temperature of the gas inside the vessel, and the internal wall in contact with it, obtained with our model, compared to the experimental results reported in [7]. Once again our result lies within the region spanned by the two experimental curves (the two discontinuous curves) and thus in excellent agreement with them. The plot in Fig. 1(b) shows that the temperature is driven by the cooling due to the expansion in the first stage of the depressurisation, up to c.ca 30 s. Later the heat coming in from the outside becomes important and the gas is heated up by the walls. For large $t$, the temperature goes back to equilibrium with the external environment and the pressure stops dropping.

The numerical results obtained by our model, of the temperature evolution of the wall surface in contact with the gas (see Fig. 1b), are again in excellent agreement with the experimental data, as our prediction lies between the two experimental curves.

## 3.2  Experiment S9

In this experiment, we model a cylindrical vessel of 1.130 m diameter, 3.240 m length, 5.9 cm wall thickness and top choke of 1 cm diameter. The initial composition is of 85.5 mole % methane, 4.5 mole % ethane, 10.0 mole % propane, at 120 bara and 290.15 K. The vessel is immersed in stagnant air at 290.15 K.

The pressure evolution predicted by our model is reported in Fig. 2(a). As we
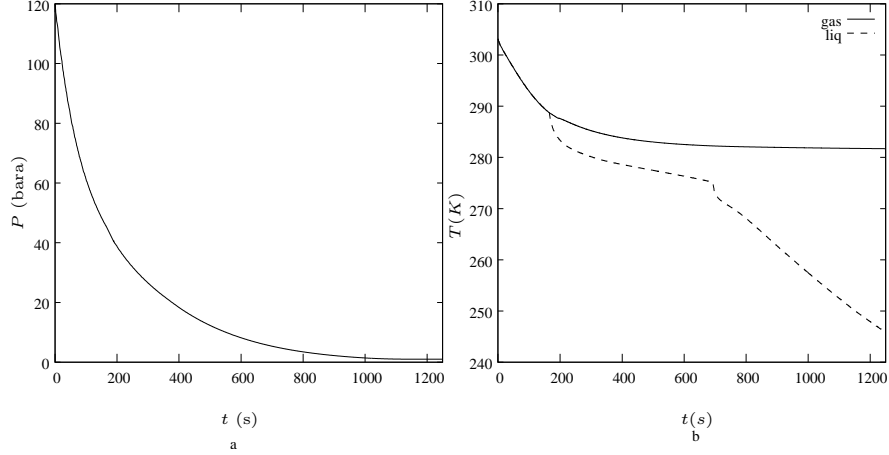


Fig. 2: a): Pressure evolution of experiment S9 against time. The pressure decrease is again almost exponential and rather close to the results reported in the paper by Haque and co-workers. b): $T$ evolution of the wall in contact with the two fluids. After the liquid appears (see text), the wall in contact with it cools much more rapidly than the wall in contact with the gas as is expected.

can observe from Fig. 2(a), the pressure drop is rather slower than in experiment I1. This is probably due to the less efficient expansion of the heavier hydrocarbons in the parent, and the lower value of the initial pressure. As a consequence, the temperature of the wall in contact with the gas (see below), although slowly, drops rather more significantly than in the previous example.

In Fig. 3(a), we show the temperature evolution of the fluid inside the vessel. Liquid appears after about 165 s from the start of the blowdown, with some delay, after the crossing of the phase boundary. This delay is probably due to the rapidity of the blowdown process, that makes the phase transition occur in the "spinodal region", *i.e.*, where the parent becomes unstable [10], rather than at the "cloud point", *i.e.*, where the two phases actually start to coexist. However, this delay, although confirmed by the experimental results reported in [7], could as well be just a numerical effect. In fact, our program does not include any stability check of the free energy and the phase equilibrium equations are only solved without looking for a globally more stable solution [10]. It could well be that the liquid actually appears earlier than we found with our model. However, this aspect, although interesting, lies beyond our present scope.

Note the jump of the gas temperature after about 200 s, immediately after the appearance of the liquid phase. This abrupt increase in the temperature is due to the heat of condensation transmitted to the gas by a finite quantity of material passing into the liquid phase. Correspondingly, there is a small decrease of the liquid temperature, due to the influence of this quantity of drops at temperature $T^{\mathrm{G}} < T^{\mathrm{L}}$ falling into the liquid bulk phase. Note also the appearance of some numerical noise in later stages. These oscillations are probably due to some errors in the evaluation of the internal
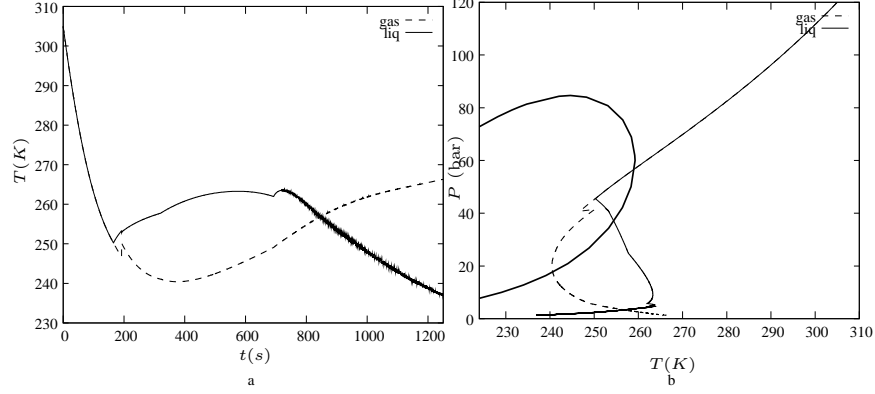
Fig. 3: (a) – Evolution of the temperature of the fluid in experiment S9. Liquid appears after about 165 s from the start of the depressurisation. The liquid is immediately heated up by the wall, due to its larger thermal conductivity, compared to the one of the gas. For large $t$, after the depressurisation is complete, the two fluids tend to have the same temperature.

(b) – $P$ against $T$ evolution of experiment S9, together with the two phase coexistence region. During the blowdown, the system enters the phase coexistence region, but only after some time, the liquid (dashed line) actually appears. Clearly, being the compositions of the two phases different and different from the parent, after that point, the phase envelope does not correspond to the phase envelope of either phase.

energy of the liquid, when the quantity of liquid becomes small due to vaporization. The temperature of the liquid appears to be rather sensitive to changes in the value of the internal energy.

The delay after which the liquid phase appears, is more evident when we plot the $P$ against $T$ evolution, together with the phase diagram relative to the initial composition (see Fig. 3(b)). The two phase coexistence region is bordered by the phase envelope (thick continuous curve in Fig. 3(b)). The $P$ vs. $T$ evolution predicted by our model during the depressurisation correctly cross the envelope (phase boundary) and the liquid appears after some delay, well inside the coexistence region.

There is also to notice, that when the liquid solution is found, we do not actually have an incipient liquid phase and a parent gas phase. In fact, the first solution with the two phases, already consists of a macroscopic presence of liquid and therefore the cloud point is already far behind and has actually been missed by our algorithm. It is possible that a more precise investigation of the onset of the phase coexistence, *e.g.*, by reversing and reducing the step to look for the point at which the liquid actually appears, would lead us closer to the phase envelope. However, again despite being scientifically an interesting point, we decided to overlook this phenomenon, and concentrate on the temperature evolution of the vessel walls.

In Fig. 2(b) we plot the temperature of the wall portions in contact with the two fluids against time. As it can be seen, the whole surface is at a certain uniform temperature when the liquid appears, as it should be, since the vessel is up to that point filled with gas only. Furthermore, since we apply "partial phase equilibrium

assumption", the liquid, when it's formed, is instantly in phase equilibrium with the gas. However, due to the abrupt change of the thermal conductivity (higher for the liquid), the liquid absorbs much more heat from the wall, and the wall in contact with it cools much more rapidly than the wall in contact with the gas. This result is expected, and confirmed by the experiments in [7]. On the other hand, the liquid is immediately heated up by the wall and its temperature rises abruptly after its formation, above the temperature of the gas.

Furthermore, the strong cooling of about 50 K experienced by the wall in contact with the liquid is again excellent agreement with the experimental and numerical results shown in [7]. Finally, at present, we have no physical explanation for the sudden change in the steepness of the temperature in contact with the liquid at about 700 s, and corresponding to a similar change in the temperature of the liquid. This jump in the derivatives corresponds to a big discontinuity of the viscosity of the liquid phase, that suddenly jumps down of two orders of magnitude to become similar to the viscosity of the gas. This is probably a non physical behavior, induced simply by the model for the viscosity, which based on the description of the models by Ely and Hanley [4, 5]. Further investigations are being carried out.

## 4   Conclusions

We presented a model for the blowdown of pressure vessels containing a mixture of hydrocarbons. Our model is based on a global mass and energy balance between the phases, gas and occasionally liquid, present in the vessel, at every stage of the blowdown. The strong cooling to which the vessel wall may be exposed, especially in presence of some liquid, requires an accurate modelling which takes into the account as many phenomena as possible, in order to avoid cracks in the vessel. Our model, which is based on a compositional approach, allows for the presence of many different hydrocarbons within the vessel, as well as non-equilibrium conditions between the phases. All the heat exchanged between the fluids and with the external environment, via heat diffusion across the vessel walls are also considered. In order to account for the mass and energy exchanged between the phases, a partial phase equilibrium assumption has been made. Within this approximation, we assume that the phase formed by condensation and/or vaporization, remains instantly in equilibrium with its parent phase, before moving into the corresponding bulk phase and homogenizing with it.

The numerical results show a rather good agreement with some experimental results, both qualitatively and quantitatively. In particular, in the case of a mixture of methane, ethane and propane, the appearance of a liquid phase after some time from the start of the depressurisation is correctly predicted. The blowdown is estimated to be complete in about 1200 s, in line with the experiments. Also the temperature drop of the fluids and the wall in contact with them is quite well estimated by our model. Similarly, for experiment I1, consisting on the blowdown of a vessel containing $N_2$ only, the drop of the pressure and temperature of the gas and of the wall in contact with it are all in excellent agreement with the experimental results.

## Acknowledgments

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